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Xing Xing
University of New South Wales, x.xing@unsw.edu.au

Harold P. Rogers
BlueScope Steel Research, hrogers@uow.edu.au

Guangqing Zhang
University of Wollongong, gzhang@uow.edu.au

Paul Zulli
BlueScope Steel Limited

Oleg Ostrovski
University of New South Wales, o.ostrovski@unsw.edu.au

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Abstract

Metallurgical cokes were subjected to gasification by CO-CO2-N2 gas with blast furnace-like composition-temperature profile to 1400 °C and annealing under N2 at temperature up to 2000 °C. The degradation of coke strength following reaction and annealing was characterised using tensile testing. Both gasification and annealing decreased the mechanical strength of coke. Degradation of all examined cokes by gasification at 1400 °C was stronger in comparison with annealing at the same temperature.

Keywords

subjected, furnace, gasification, conditions, coke, annealing, structure, pore, under, macrostrength, blast

Disciplines

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Macrostrength and Pore Structure of Coke Subjected to Gasification and Annealing under Blast Furnace Conditions

Xing Xing[1], Harold Rogers[2], Guangqing Zhang[3], Kim Hockings[4], Paul Zulli[2], Oleg Ostrovski[1]

[1]School of Materials Science and Engineering, UNSW Australia, NSW 2052, Australia
Phone: +61 2 9385 5120
E-mail: x.xing@unsw.edu.au

[2]BlueScope Steel, Port Kembla, NSW, 2505 Australia

[3]School of Mechanical, Materials & Mechatronic Engineering, University of Wollongong, Wollongong, NSW 2522, Australia

[4]BHP Billiton, Brisbane, QLD 4000, Australia

ABSTRACT

Metallurgical cokes were subjected to gasification by CO-CO_2-N_2 gas with blast furnace-like composition-temperature profile to 1400 °C and annealing under N_2 to 2000 °C. The degradation of cokes strength after reaction and annealing was characterised using I-drum tumbling and tensile testing. The I-drum tumble strength of the cokes after processing was considerably higher than that measured in standard CSR/CRI tests. Pore structure of cokes was examined using image analysis. Porosity and pore size were both enlarged by gasification and annealing; The pore structure change during gasification was mainly as a result of Boudouard reaction; the pore structure development upon annealing was attributed to the reactions of mineral matters with carbon and transformation within the carbon framework. The pore structure of all cokes after annealing and gasification, showed a decrease in average pore roundness and an increase in the area fraction of low roundness pores suggesting an increase in pore connectivity. Increasing volume of connected pores during annealing and gasification was a major factor causing the degradation of cokes under the simulated blast furnace conditions.

Keywords: Coke degradation, Blast furnace conditions, Macro strength, Porosity, Pore structure.

INTRODUCTION

Metallurgical coke quality is critical to all blast furnace ironmaking operations. The ultimate measurement of coke quality is its resistance to degradation under the blast furnace operating conditions. From this perspective, coke integrity is a major parameter in the development of ironmaking technology, with decreased coke consumption. Coke in blast furnace is subjected to significant mechanical stress being exposed to chemical reactions with gases (CO, CO_2, H_2) and heating to high temperature. Peak coke temperatures are of the order of 2000-2200 ^oC (typical raceway adiabatic flame temperatures). The coke is required to maintain adequate strength upon heating and reaction, and minimise fine coke generation to secure adequate burden porosity and uniform liquid and gas flows.

In an industrial practice, the "hot" strength of coke is typically determined using CSR/CRI test developed by Nippon Steel Corporation (NSC) [1]. However, the conditions of the CSR/CRI test are far from the conditions in the BF, with the CO_2 content in the CSR/CRI test (100%) significantly higher. Results from an experimental BF indicate that the CO_2 content in the BF gas at 1100 °C may only be 5 vol% [2]. Moreover, other gases in the BF gas atmosphere, such as N_2 H_2, H_2O and CO, are not present in the CSR/CRI test. Van der Velden et al. [3] compared coke reactivity and strength after reaction using the standard CSR/CRI test with test results obtained under conditions simulating BF gas and temperature. The weight loss in the CSR/CRI test was higher than that under BF conditions and the strength of coke after reaction was independent of the extent of reaction [3]. Lundgren et al. [2] observed that in the CSR/CRI test, the degradation had progressed throughout the whole coke lump, whilst under BF conditions, it was limited to the peripheral layer. The strength of coke after reaction under BF conditions was considerably higher than that in the CSR/CRI test.

The effect of heating on the coke strength was studied previously [4-7]. Grant et al. [4] observed an increase in coke compressive strength when tested at 1400 °C. Patrick et al. [5] found that the tensile strength of coke tested at 1450 °C was lower than that at ambient temperature. Xing et al. [6, 7] examined the effect of annealing of cokes, chars and pyrolysed coals in the temperature

range of 700 to 1500 °C on tensile strength measured at room temperature. The tensile strength of chars and pyrolysed coals wasstrongly enhanced by annealing in the temperature range of 700-1100 °C. The tensile strength of cokes was slightly decreased by the heat treatment after the annealing temperature increased above 1300 °C. Coke degradation upon heating to temperatures close to the raceway flame temperature was not studied.

The strength of highly porous and brittle materials like coke depends on its pore structure and properties of wall component [7-10]. Therefore the degradation of coke in the blast furnace ironmaking is related in part to the change of pore structure upon blast furnace thermal and reaction conditions. Pore structure of coke has been intensively studied with a focus on its development during the pyrolysis process [11-20]. However, the development of pore structure of metallurgical coke under the blast furnace conditions has not been systemically investigated.

The aim of this paper is to quantify the degradation of coke strength and pore structure upon reaction under conditions simulating blast furnace gas composition-temperature profiles to 1400 °C and annealing under N_2 to 2000 °C, and develop an understanding of the mechanism of coke degradation in blast furnace ironmaking.

EXPERIMENTAL

Materials

Three metallurgical cokes A, C and D, were studied in this work. Coke A was produced from a medium volatile base blend of moderate inertinite content (36.9 vol%) with addition of 11 wt% semi-soft coal. Cokes C and D were pilot oven cokes prepared from low rank and high rank coals, respectively. A summary of coke proximate analyses and results of CSR/CRI tests are presented in ***Table 1***. All coke samples used in this work were +19 and -21 mm in size and were prepared using same method as the standard CSR/CRI test.

Table 1. Proximate and CSR/CRI analyses of coke samples

	Coke A	Coke C	Coke D
Moisture content* M_{ad}, %	0.4	0.5	0.9
Volatile matter* V_{ad}, %	1.4	1.5	0.3
Ash* A_{ad}, %	11.9	12.1	11.8
CSR, %	70.2	62.7	31.9
CRI, %	20.7	24.6	46.7
Volatile matter of parent coal (blend)* V_{parent}, %	24.5	18.0	27.0

* Air dry basis.

Annealing and gasification of cokes

Annealing

200 g of coke with a particle size of +19-21 mm was heat-treated in a graphite furnace for 2 hours at temperatures of 1400, 1600, 1800, and 2000 °C under the 100% N_2 atmosphere. The heating rate to the nominated treatment temperature was fixed at 25 °C/min. The samples were contained in a graphite crucible, into which 1 L/min of nitrogen (99.99%) was continuously blown through a graphite ducting tube attached to the bottom of the crucible. Heat treatment time was counted from the time when the furnace temperature reached the designated value. The feed coke sub-sample was labelled as Coke 1. The four coke samples, after annealing at temperatures from 1400 to 2000 °C, were labelled sequentially as Coke 2 to Coke 5.

Gasification

200 g sample of coke, contained in a silicon carbide reaction vessel, was reacted under conditions simulating the blast furnace gas composition-temperature profile from 900 to 1400 °C. The gas composition-temperature profile was based on a vertical probing of the blast furnace measurement after van der Velden et al. [3]. In the current experiments, water and hydrogen were excluded from the gas atmosphere and the total gas flow rate was fixed at 5 L/min. The temperature increment between 900 and 1000 °C corresponded to the coke passage through the furnace thermal reserve zone, and from 1100 to 1400 °C approximated to its passage through the cohesive or softening-melting zone. The composition of CO-CO_2 with balance N_2 gas mixture varied with temperature according to the atmosphere in the different regions of the blast furnace as shown in ***Figure 1***. The gasification started at 900 °C and stopped once temperature reached 1000 °C, (Coke 6), 1200 °C, (Coke 7) and 1400 °C, (Coke 8). For Coke 9, the gasification was again followed to 1673 K (1400 °C) and then the sample was held at this final condition for 2 additional hours. Coke samples were quenched under N_2 after the gasification reaction.

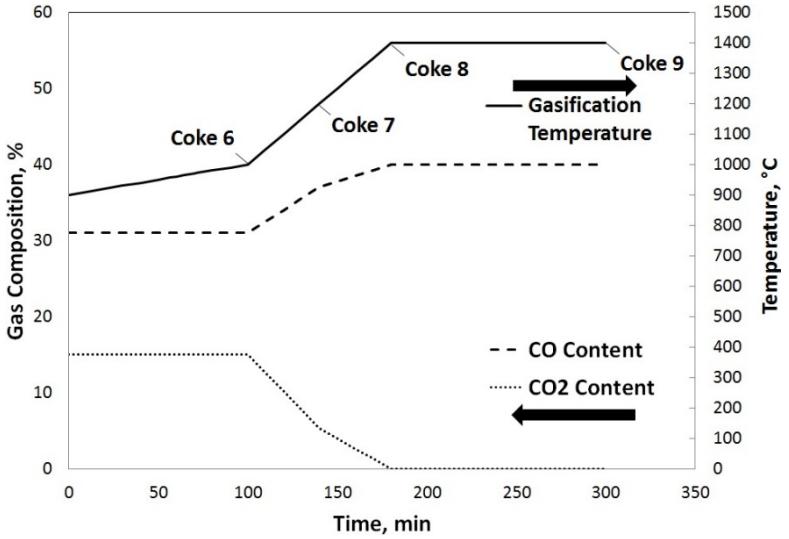

Figure 1. Gas composition-temperature profile of gasification

Strength of metallurgical cokes

Tensile strength

Tensile strength of cokes was tested on an **Instron 1185** screw universal testing machine. For the 8mm (diameter) by 8 mm long prepared coke pellets the tensile strength, σ was calculated using equation (1) below:

$$\sigma = \frac{2P}{\pi dl} \quad (1)$$

where ***P*** is load at sample failure and ***d*** and ***l*** are diameter and thickness, respectively.

Coke strength after reaction

The strength and weight loss of cokes after reaction under the simulated blast furnace conditions were evaluated using the procedure similar to the standard CSR/CRI testing [1]. The weight loss of samples treated under different conditions was calculated. A sub-sample of the treated coke (150 $\pm$ 2.5g) was tumbled in an I-drum tumbler rotated at 20 r/min for 30 minutes. The tumbled sample was sieved over a 10 mm perforated plate laboratory sieve; the fraction (%) of +10mm of the original samples was reported as the strength after reaction and designated as I^{*}_{600}.

Porosity and pore structure

Pore structure and size in cokes subjected to gasification and annealing was investigated using image analysis. A representative analysis of each coke was based on 60 images of 60 samples from each condition which were mounted in epoxy resin blocks. Images were captured by a Nikon Model EPIPHOT 600 microscope with Nikon digital camera. Since the large pores were of most interest in connection to coke degradation, a low power objective lens (magnification ×5) was used. In this configuration, small pores (< 12 μm) were not resolved.

The captured images were binarised using software ImageJ developed by NIH. After binarisation, the pores and walls of cokes were represented by black and white areas respectively. The porosity of carbonaceous materials was calculated using ImageJ as the fraction of black area.

Parameters of pore geometry, including mean area, perimeter and equivalent circle diameter, were determined by LAS Image Analysis software developed by Leica. Analysis of each coke was based on 10 images of 10 samples mounted in epoxy resin blocks. Roundness of pore R was calculated using measured pore area and perimeter [21]

$$R = \frac{4\pi S}{L^2} \quad (2)$$

where S and L are the area and perimeter of a pore, respectively. The maximum roundness of pore is 1 in the case of circle; it decreases with increasing complexity of the pore shape. ***Figure 2*** presents images of pore structure with roundness 0.7 and 0.2. The coke with high pore roundness tends to have individual pores with shape close to circle; the pore structure of coke with low pore roundness is consisted of the connected pores with complicated shape, in addition, the pore walls seem to be discontinuous (Figure 2). The area fraction of pores with roundness threshold $\leq$ 0.1was attempted and calculated using the pore geometry parameters of each pore measured with LAS Image Analysis software.

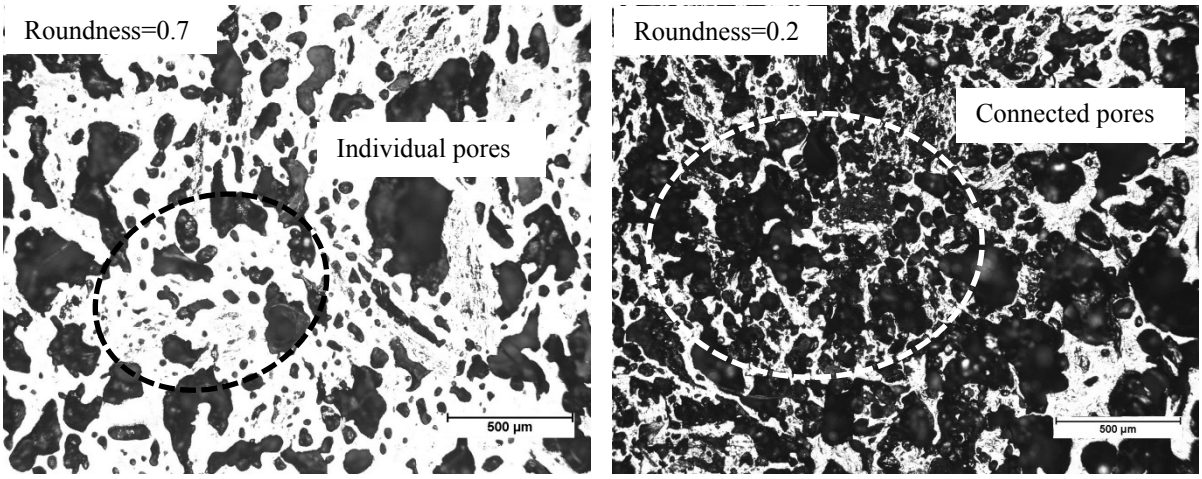

Figure 2. Pore structure of coke with different pore roundness

X-ray diffraction

Mineral phases in cokes were identified using X-ray diffraction (XRD) analysis. Cokes were crushed to passing 212 µm then ashed by heating in air at 815 °C to remove carbon. XRD spectra were obtained using a Philips X'Pert Multipurpose X–ray Diffraction System (MPD). Copper Kα radiation (45 KV, 40 mA) was used as the X–ray source. Samples were scanned with 2θ in the range of 10 to 70° with a step size of 0.02° and 0.6 s scanning time at each step. Mineral phases were identified using X'Pert HighScore Plus software.

RESULTS AND DISCUSSION

Reactions of cokes during annealing and gasification

A series of reactions took place when the coke samples were treated at high temperatures either in nitrogen or in a simulated blast furnace gas atmosphere which resulted in weight loss of samples. The weight loss of coke samples after annealing and gasification to different stages is shown in ***Figure 3***. The weight loss of all the cokes subjected to annealing and gasification increased with increasing treatment temperature. The weight loss of cokes during annealing in a nitrogen atmosphere resulted from loss of moisture and volatile matter (proximate), further devolatilisation at high temperatures, and reduction of oxides in mineral matter by encapsulating coke carbon. During the gasification process when CO_2 was present in the gas phase, the solution loss reaction made a significant contribution to the weight loss; beside the Boudouard reaction, release of moisture and volatile matter and the mineral reaction at temperature below 1400 °C also contributed the weight loss.

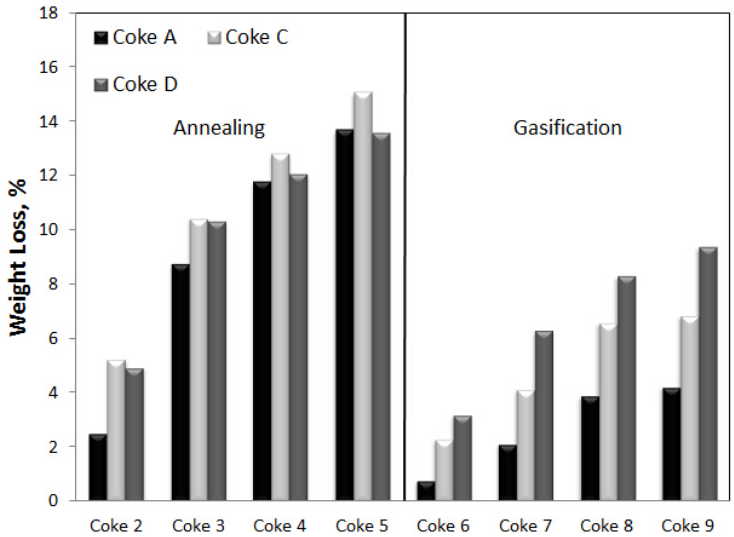

Figure 3. Weight loss of cokes after annealing and gasification to different stages

From Figure 3, the weight losses of Cokes A and C after gasification to 1000 °C, (Coke 6) were equivalent or lower than the sums of their individual moisture and volatile matter (proximate), which means that the solution loss reaction was insignificant at this stage. Coke D had a higher weight loss than that of A and C, although its sum of moisture and volatile matter was smaller. This higher weight loss for Coke D remained for other gasified samples, indicating that Coke D was more reactive to CO_2. After gasification to 1400 °C, the weight loss of Coke 8 was higher than corresponding annealed samples at the same temperature (Coke

2). When the treatment process was extended for an extra 2 hours at the same temperature without CO_2 provided in the gas phase (Coke 9), the weight loss increased further especially for Coke D, showing that most of weight loss at high temperatures was caused by carbothermal reduction of the metal oxides in the mineral matter (mainly SiO_2) of coke.

Increasing the annealing temperature from 1400 °C (Coke 2) to 2000 °C (Coke 5) brought about an increase in the weight loss of 8-11% for all three cokes. This significant increase is related to the rearrangements in the carbon framework and the reduction of mineral matter. Carbothermal reduction of SiO_2 to SiO and SiC significantly contributed to the weight loss at high temperatures [6]; the reaction of other minerals with low content, such as Fe bearing minerals, also made contribution to the weight loss during annealing [22].

For all three cokes, the weight loss of samples subjected to gasification (Cokes 6-9) was considerably lower than for the standard CSR/CRI test (Table 1). No correlation was observed between the coke weight loss in annealing experiments and the CRI value. However, the weight loss of cokes in the gasification and CSR/CRI test were correlated, i.e. cokes with higher CRI had a higher weight loss under the simulated blast furnace conditions.

Porosity of cokes during annealing and gasification

The porosity of the original cokes and cokes treated under the simulated blast furnace conditions is presented in ***Figure 4***. Original Coke C had the highest porosity of 66.3%, while the porosities of original Cokes A and D were 51.1 and 57.9%. Annealing in the temperature range of 1400-2000 °C caused the porosity evolution of all cokes. The porosity of Cokes A, C and D after annealing at 2000 °C increased by 16.5, 9.5 and 6.0%, respectively.

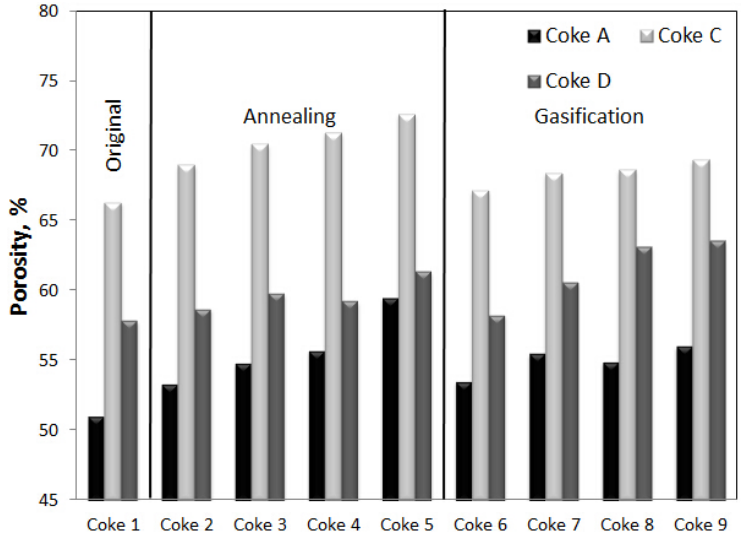

Figure 4. Porosity development of cokes subjected to annealing (samples 2-5) and gasification (samples 6-9) under the simulated blast furnace conditions

Comparing porosity of samples 9 subjected to gasification to 1400 °C and samples 2 annealed under N_2 at the same temperature, it can be concluded that the gasification had a greater effect on porosity development, most notably in the case of Coke D. Annealing of Cokes A and C in the temperature range 1600-2000 °C caused more significant enlargement of coke porosity than that in gasification treatment. However, the porosity of Coke D after gasification at 1400 °C was 63.6% which was slightly (3.5%) higher than its porosity after annealing at 2000 °C.

Weight loss of coke during annealing was caused by the release of moisture and volatile matters, further devolatilisation at high temperatures as well as reaction of mineral matter with carbon; while, the Boudouard reaction, release of moisture and volatile matter, and the mineral reaction occurs at temperature below 1400 °C were the main reasons of weight loss of coke during gasification. ***Figure 5*** shows correlation of weight loss and porosity of cokes subjected to annealing and gasification.

The porosity of cokes was enlarged with increasing weight loss during both annealing and gasification. During annealing at 1400 to 2000 °C, the increase of weight loss of Coke A with increasing annealing temperature was most significant among the three cokes. After annealing at 2000 °C, the weight loss of Coke A was 13.7% which was 4.5 times higher than the weight loss of Coke A annealed at 1400 °C. Correspondingly, the porosity of Coke A increased after annealing at 2000 °C by 16.5 % compared with original coke, which was more significant than that of Coke C and D. In the gasification, Coke D was more reactive to CO_2, and the porosity development of Coke D was more notable during gasification.

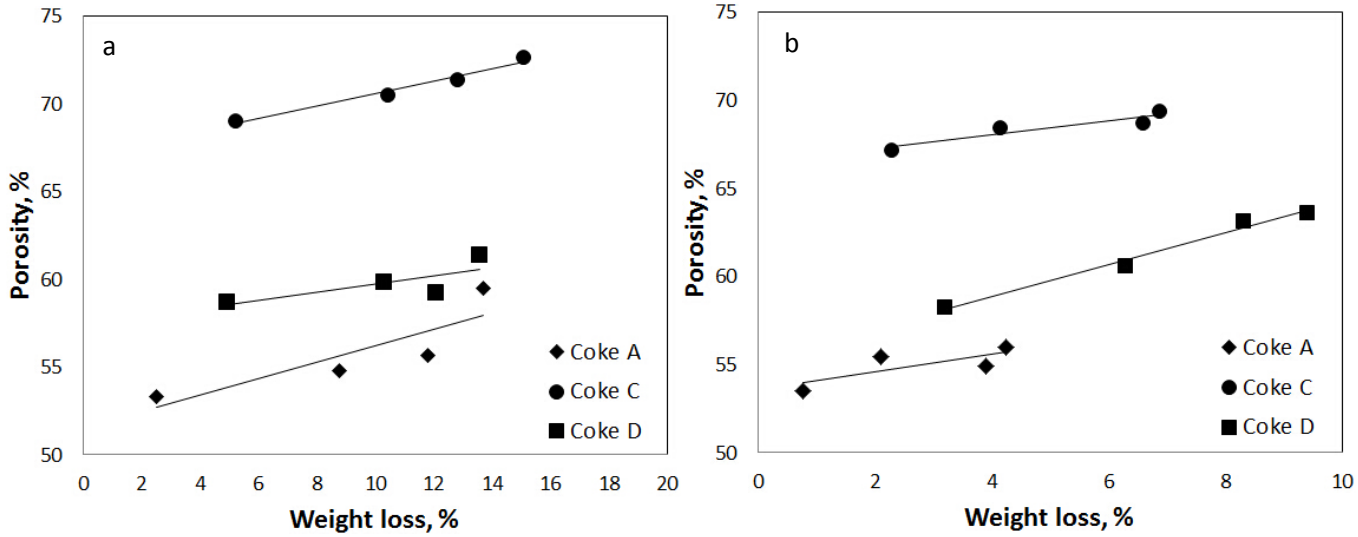

Figure 5. Correlation between porosity and weight loss during annealing and gasification (a) Annealing (b) Gasification

Development of pore structure of cokes during annealing and gasification

Parameters of the pore structure of cokes before and after processing under the simulated blast furnace conditions were determined using image analysis. Development of the pore structure is of significant interest in relation to the coke mechanical properties. Only pores with a size over 1000 μm^2 were considered as smaller pores do not have a significant effect on the mechanical properties of metallurgical cokes [23].

The pore mean area, perimeter, equivalent circle diameter, average pore roundness, and area fraction of pores with roundness ≤ 0.1, are presented in ***Table 2***.

Table 2. Parameters of the pore geometry of cokes subjected to annealing and gasification under simulated blast furnace conditions

	Mean area*, μm^2	Perimeter, μm	Equivalent circle diameter, μm	Average pore roundness	Area fraction of pores with roundness ≤0.1, %
Coke A1	16304	527	108	0.74	2.7
Coke A2	19457	605	115	0.67	8.9
Coke A5	25068	778	118	0.52	21.8
Coke A9	26095	675	126	0.72	12.2
Coke C1	16817	762	103	0.36	29.3
Coke C2	35423	1205	127	0.31	46.6
Coke C5	69871	2254	138	0.17	59.9
Coke C9	48601	1490	128	0.28	53.0
Coke D1	18760	599	110	0.66	13.0
Coke D2	19268	647	112	0.58	14.2
Coke D5	21175	750	115	0.47	26.2
Coke D9	35119	886	127	0.56	35.7

* Only pores with an area of more than 1000 μm^2 were included in this table

The average pore diameter of three cokes was in the range of 103-110 μm; it was similar for all three cokes. Annealing at temperatures 1400 to 2000 °C enlarged the average pore size. The effect of annealing was more significant on Coke C than on Cokes A and D. Coke C before treatment had the smallest pore diameter, which increased after annealing at 2000 °C by approximately 34%. Gasification of all cokes at 1400 °C had a stronger effect on the pore size than annealing at the same temperature; the effect was more evident for Coke D, which pore size after gasification at 1400 °C was 13% larger than after annealing at the same temperature.

Average pore roundness and area fraction of pore with low roundness were calculated based on the measurement of pore area and perimeter. Original Coke A had the highest average pore roundness, 0.74, and the lowest area fraction of low roundness pores, 2.7%. The pore structure of original Coke A mainly consisted of single pores with shape close to circle; while, the pores of original Cokes C and D were with a more complicated shape. Images of pore structure of cokes before and after processing are shown in ***Figures 6*** to ***8***. During annealing process, the average pore roundness of all cokes decreased and the volume of low roundness pore increased as the annealing temperature rose. Significant change of average pore roundness and volume of low roundness pore were observed for Cokes A and C (Figures 6 and 7). Comparing with Cokes A and C, the change of pore structure of Coke D in annealing was less significant (Table 2 and Figure 8).

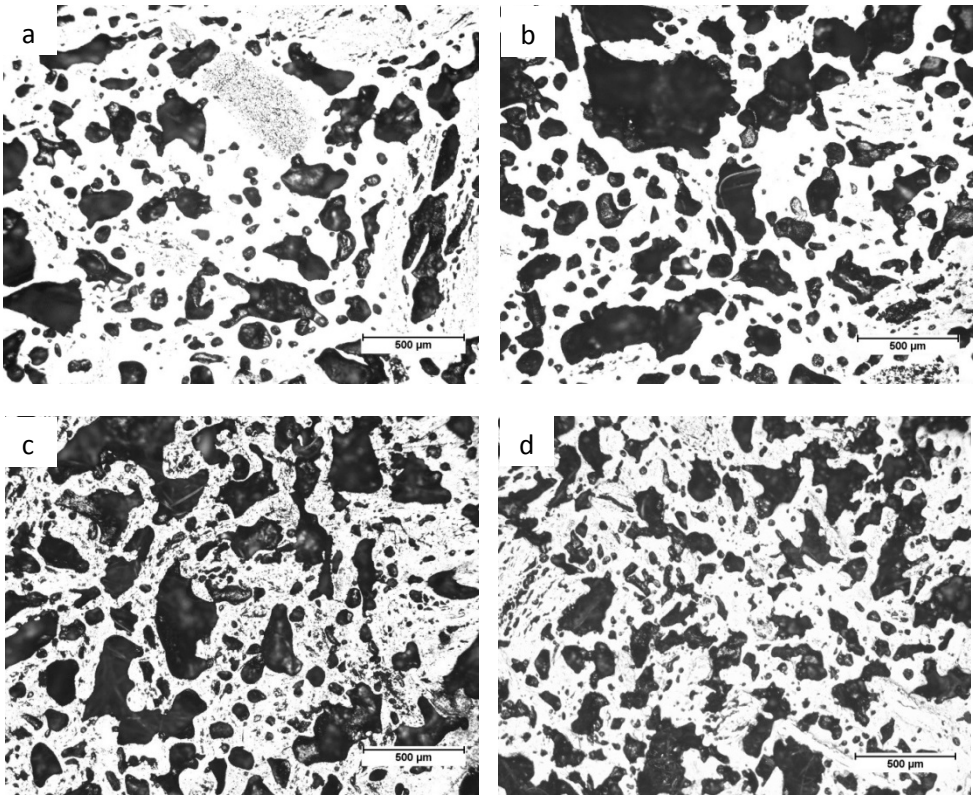

Figure 6. Coke A before and after processing under simulated blast furnace conditions (a) Original coke (b) Annealed at 1400 °C for 2h (c) Annealed at 2000 °C for 2h (d) Gasified at 1400 °C for 2h

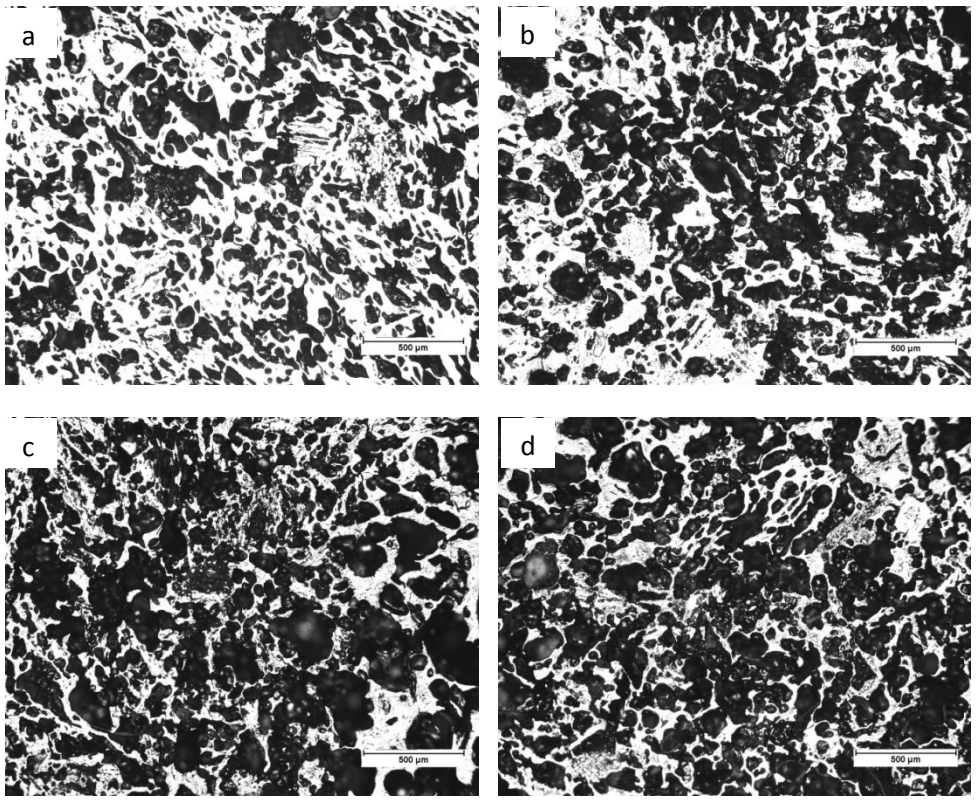

Figure 7. Coke C before and after processing under simulated blast furnace conditions (a) Original coke (b) Annealed at 1400 °C for 2h (c) Annealed at 2000 °C for 2h (d) Gasified at 1400 °C for 2h

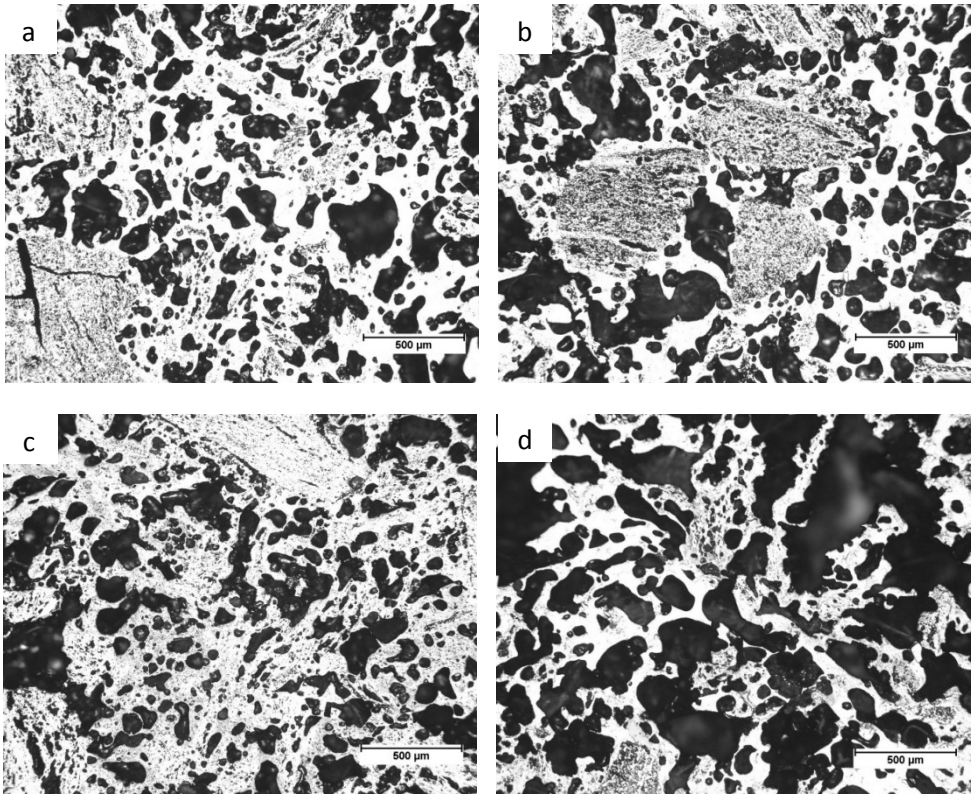

Figure 8. Coke D before and after processing under simulated blast furnace conditions (a) Original coke (b) Annealed at 1400 °C for 2h (c) Annealed at 2000 °C for 2h (d) Gasified at 1400 °C for 2h

Gasification of cokes at 1400 °C for 2 hours increased the volume of low roundness pores of all three cokes and decreased their average pore roundness. These data indicate that some pores became connected after gasification [21]. Effect of gasification at 1400 °C on pore structure of cokes was more significant than annealing at the same temperature but smaller than annealing at 2000 °C except of Coke D. Gasification made considerable change in the pore structure of Coke D due to its high reactivity; after the gasification at 1400 °C for 2 hours, the low roundness pore volume of Coke D was 1.5 times larger than after annealing at 1400 °C and 36% larger than after annealing at 2000 °C.

Macrostrength of cokes during annealing and gasification

Tensile strength

The tensile strengths of original cokes and cokes after annealing and gasification are presented in ***Figure 9***. Among the three coke samples, Coke A had the highest tensile strength of 7.71 MPa, while for Cokes C and D the measured values were 4.62 and 5.49 MPa, respectively. For all three cokes, the tensile strength decreased with increasing annealing temperature; an approximately 38% decrease in the tensile strength was observed for Cokes A and C on annealing at 2000 °C and a smaller, 12%, decrease in the case of Coke D. This smaller decrease in tensile strength of Coke D corresponds to a smaller increase in the graphitisation degree of the same coke due to annealing.

The extent of gasification negatively affected the tensile strength of cokes, which decreased with increasing gasification temperature. Compared with annealing at 1400 °C (Coke 2), gasification at same temperature (Coke 8 and 9) had a more significant effect on the degradation of coke strength. The tensile strength of Coke A decreased by about 8% after gasification until 1000 °C, and then changed marginally with further increases in gasification temperature. Gasification had a stronger effect on the tensile strength of Coke D, which was opposite to the case of Cokes A and C. The tensile strength of Coke D after gasification at 1400 °C, (Cokes 8 and 9) was lower than after annealing at 2000 °C.

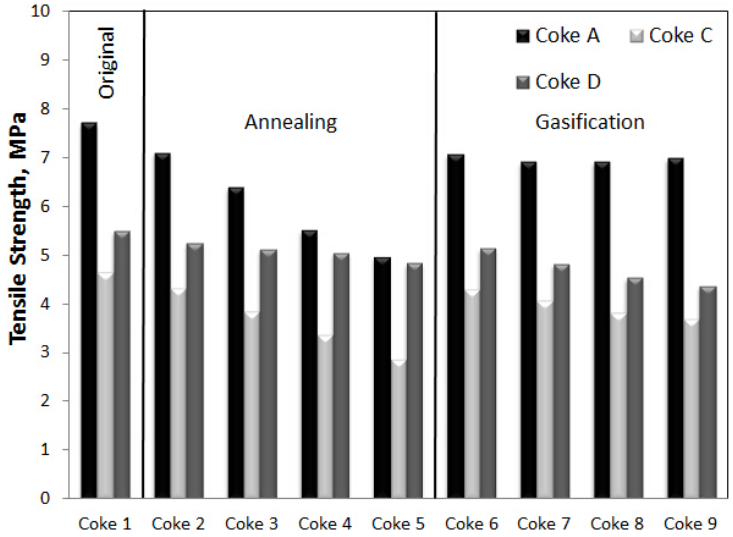

Figure 9. Tensile strength of cokes subjected to annealing and gasification

Coke strength after reaction

Coke strength after treatment under the simulated blast furnace conditions determined through I-drum tumble testing, I^*_{600}, is shown in ***Figure 10***. Original Coke A had the highest I-drum tumbling strength, while I^*_{600} of Coke C was the lowest before treatment. It should be noted that results of I^*_{600} tests do not correlate with the standard CSR test. The coke strength after gasification under simulated blast furnace conditions, I^*_{600}, was much higher than the CSR from the standard test, particularly for Coke D. The standard CSR/CRI test is executed with a more aggressive gaseous atmosphere of 100% CO_2; the CO_2 content of the simulated blast furnace atmosphere applied in the current tests was 5.3 vol% at 1200 °C and decreased linearly to 0% at 1400 °C.

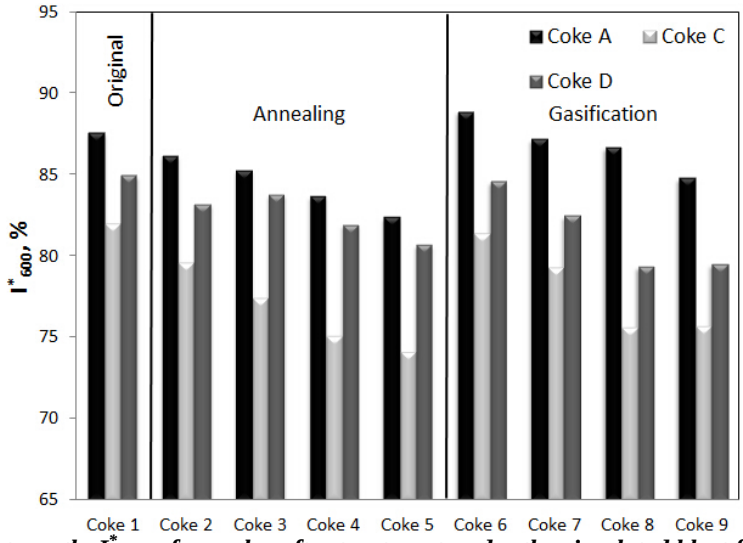

Figure 10. Coke strength, I^*_{600}, of samples after treatment under the simulated blast furnace conditions

Factors affecting pore structure during annealing and gasification

In the gasification process, the enlargement of porosity and connection of individual pores was mainly caused by the Boudouard reaction:

$$C_{(s)} + CO_{2(g)} = 2CO_{(g)}, \quad \Delta G^0 = 162.31 - 0.1691T \tag{3}$$

Beside the Boudouard reaction, release of moisture and volatile matter, and the mineral reaction occurs at temperature below 1400 °C also contributed the change of pore structure during gasification.

During annealing process, the change of pore size and structure of coke was predominantly attributed to the reaction of minerals with carbon. Furthermore, at elevated temperatures, the transformation within carbon framework can also contribute to connection of pores. XRD spectra of ash of cokes annealed under the blast furnace conditions are presented in ***Figure 11***. Hematite Fe_2O_3 in the ash of annealed coke was formed by the re-oxidation of iron in the ashing process.

The XRD pattern showed that the major (crystalline) phase of mineral matter in the original coke was quartz SiO_2; small amounts of mullite $Al_6Si_2O_{13}$, rutile TiO_2 and hematite Fe_2O_3 were also detected. After annealing at 1400 °C, silicon carbide SiC and a small amount of silicon nitride Si_3N_4 were formed according to reactions:

$$SiO_{2(s)} + 3C_{(s)} = SiC_{(s)} + 2CO_{(g)},\ \Delta G^0 = 590.4 - 0.3301T \quad (4)$$

$$3SiO_{2(s)} + 6C_{(s)} + 2N_{2(s)} = Si_3N_{4(s)} + 6CO_{(g)},\ \ \Delta G^0 = 1260.1 - 0.6923T \quad (5)$$

After annealing at 2000 °C, silicon carbide SiC was the major phase in the coke, aluminium nitride AlN was also observed in the XRD pattern. Silicon nitride Si_3N_4 is unstable relative to SiC and decomposed at this temperature.

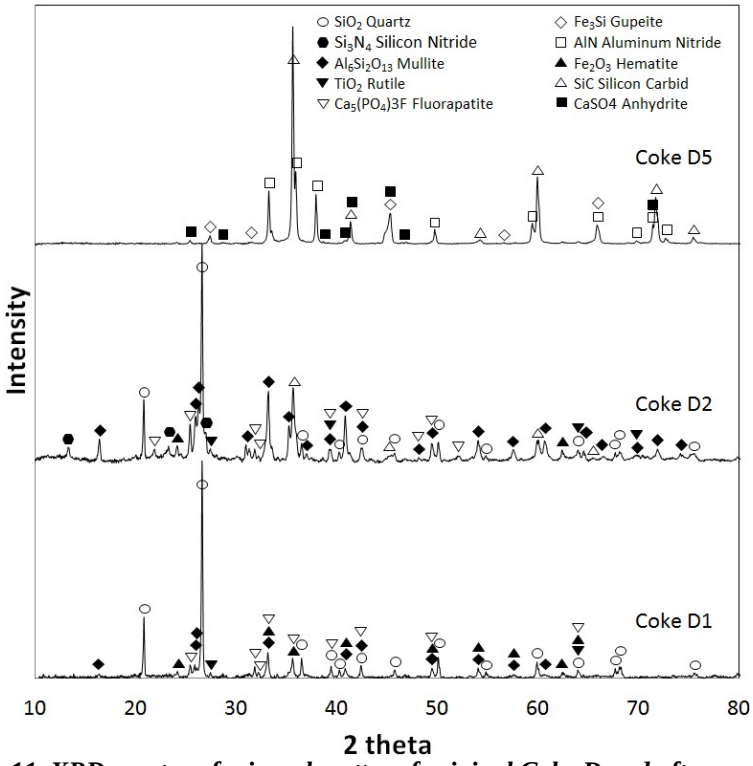

Figure 11. XRD spectra of mineral matter of original Coke D and after annealing

Partial pressure of N_2 in the annealing of coke was 1 atm. The equilibrium partial pressure of CO in reactions (4) and (5) are shown in ***Figure 12***. At temperatures below 1427 °C, calculated equilibrium partial pressure of CO in reaction (4), $P_{CO(4)}$, is lower than it is in reaction (5), $P_{CO(5)}$, which indicates that Si_3N_4 is thermodynamically a more favourable product than SiC at temperatures below 1427 °C. The $P_{CO(4)}$ and $P_{CO(5)}$ values which are 0.254 and 0.294 atm, respectively at 1400 °C indicate that reactions (4) and (5) are thermodynamically possible at this temperature. The equilibrium partial pressures of CO in reaction (4) and (5) at 2000 °C increase to 68.8 and 15.9 atm, respectively. However, at 2000 °C, silicon nitride Si_3N_4 is not thermodynamically stable and decomposes, only high concentration of silicon carbide SiC was determined in the ash of cokes annealed at this temperature.

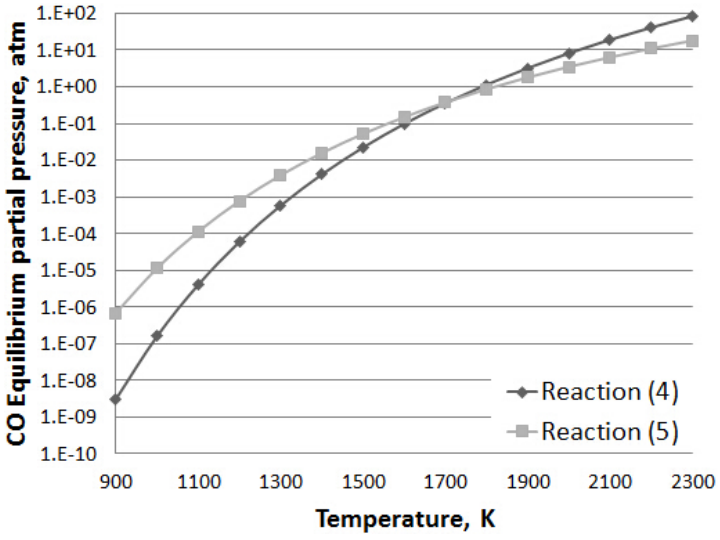

Figure 12. Equilibrium partial pressure of CO vs temperature in reactions (4) and (5)

Relationship between coke strength and pore structure

Original coke A had the highest strength while coke C the lowest among examined cokes. The tensile strength of original Coke C was 40% lower than the strength of original Coke A. The pore structure of original Coke C mainly consisted of the pores connected to each other while the original Coke A had higher fraction of single pores with shape close to the circle. Correlation between the area fraction of low roundness pores and average roundness of cokes with coke strength was examined in ***Figure 13***. Both tensile strength and I-drum tumbling strength of cokes decreased with increasing volume of low roundness pores and the decrease of the average pore roundness. These indicate that the coke strength decreased when the pore structure changed to possibly more connectable network; coke with complicated pore structure had a higher level of defects which concentrated stress than the circular individual pores. During annealing and gasification under the blast furnace conditions, the degradation of the coke strength could be attributed, in part, to the change of the coke pore structure.

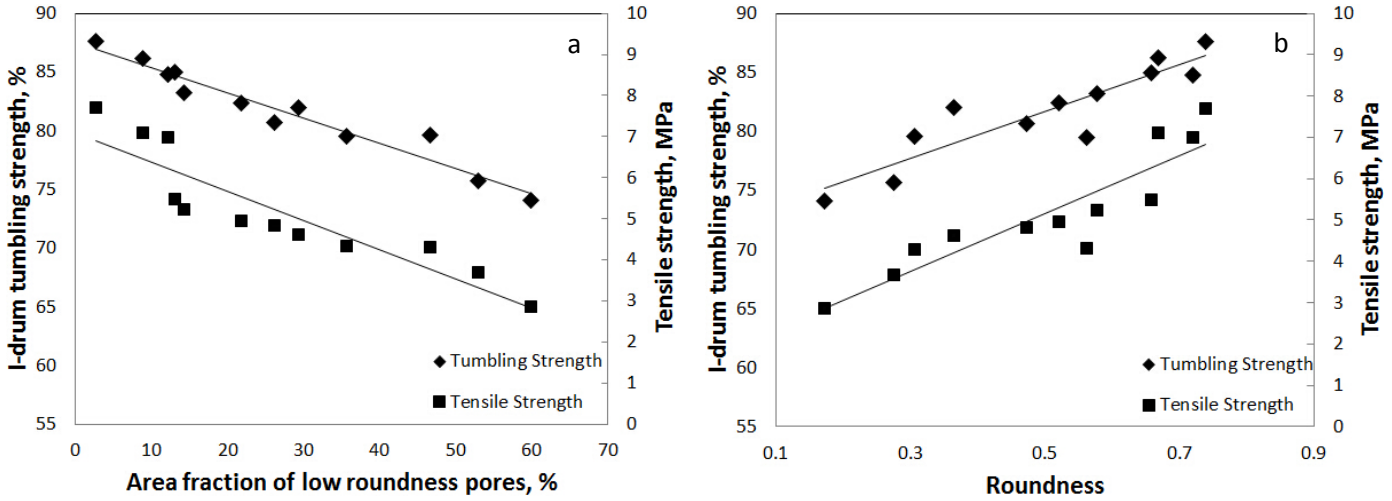

Figure 13. Correlation between coke strength and pore structure (a) Area fraction of low roundness pores (b) Average pore roundness

CONCLUSIONS

The degradation of cokes was studied under simulated blast furnace conditions which included annealing under N_2 to 2000 °C and gasification with simulated blast furnace gas composition-temperature profiles to 1400 °C. The major findings can be summarised as follows:

1. Coke strength after treatment under simulated blast furnace conditions was significantly higher than reported in the CSR/CRI test.

2. Both gasification to 1400 °C and annealing in the temperature range of 1400-2000 °C enlarged the porosity and pore size of cokes. Compared with annealing at 1400 °C, gasification at the same temperature caused more significant enlargement of coke porosity and size. The porosity development and pore enlargement of most reactive coke D upon gasification at 1400 °C was slightly higher than after its annealing at 2000 °C.

3. Pores of all cokes after annealing and gasification, showed a decrease in average pore roundness and an increase in the area fraction of low roundness pores suggesting an increase in pore connectivity. Effect of gasification at 1400 °C on the possible increase in pore connectivity was more significant than annealing at same temperature but smaller than annealing at 2000 °C except coke D with higher reactivity.

4. The pore structure changes of cokes during gasification was mainly as a result of Boudouard reaction; furthermore, release of moisture and volatile matter, and the mineral reaction occurs at temperature below 1400 °C also contributed to the change of pore structure during gasification. While the pore structure development upon annealing could be attributed to the reactions of mineral matter with carbon and degradation of carbon framework at extreme thermal conditions. The degradation of cokes upon gasification and annealing under the blast furnace conditions could be attributed to the decrease of pore roundness and increase in area proportion of low roundness pores.

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REFERENCES

1. AS, *Methods for the analysis and testing of coal and coke Part 13: Tests specific to coke*, 1990, Standards Australia.
2. M. Lundgren, L. Sundqvist Ökvist, and B. Björkman: *steel research international*, 2009, vol. 80, no. 6, pp. 396-401.
3. van der Velden, T. B., C. J., and v.d.B. R., J.,, *Coke Reactivity Under Simulated Blast Furnace Conditions*, in *58th ISS-AIME Ironmaking Conference,*1999: Chicago. p. 275 – 285.
4. M.G.K. Grant, A.C.D. Chaklader, and J.T. Price: *Fuel*, 1991, vol. 70, no. 2, pp. 181-188.
5. J.W. Patrick and H.C. Wilkinson. *High temperature properties of metallurgical coke*. in *AIME Ironmaking Conference*. 1983. Atlanta.
6. X. Xing, G. Zhang, M. Dell'Amico, G. Ciezki, Q. Meng, and O. Ostrovski: *Metallurgical and Materials Transactions B*, 2013, vol. 44, no. 4, pp. 862-869.
7. X. Xing, G. Zhang, M. Dell'Amico, G. Ciezki, Q. Meng, and O. Ostrovski: *Metallurgical and Materials Transactions B*, 2013, vol. 44, no. 4, pp. 870-877.
8. J.W. Patrick and A. Walker: *Carbon*, 1989, vol. 27, no. 1, pp. 117-123.
9. M.G.K. Grant, A.C.D. Chaklader, and J.T. Price: *Fuel*, 1991, vol. 70, no. 2, pp. 181-188.
10. S.Y. Kim and Y. Sasaki: *ISIJ International*, 2010, vol. 50, no. 6, pp. 813-821.
11. D. Hays, J.W. Patrick, and A. Walker: *Fuel*, 1976, vol. 55, no. 4, pp. 297-302.
12. J. Tomeczek and S. Gil: *Fuel*, 2003, vol. 82, no. 3, pp. 285-292.
13. P.K. Singla, S. Miura, R.R. Hudgins, and P.L. Silveston: *Fuel*, 1983, vol. 62, no. 6, pp. 645-648.
14. A. Strugala: *Fuel*, 2002, vol. 81, no. 9, pp. 1119-1130.
15. S. Nomura and K.M. Thomas: *Fuel*, 1996, vol. 75, no. 2, pp. 187-194.
16. R.J. Gray and P.E. Champagne, *Petrographic characteristics impacting the coal to coke transformation*, in *47th Ironmaking Conference*1988: Toronto. p. 313-324.
17. H. Iwakiri, T. Kamijo, I. Kobayashi, and M. Kitamura, *A fundamental study in new carbonization process at medium temperature for metallurgical coke*, in *Ironmaking Conference Process*1992: Toronto, Ontario. p. 581-586.
18. J.P. Graham and H.C. Wilkinson, *Coal properties, charge preparation and their influence on coke quality*, in *Ironmaking Conference Proceedings*1978. p. 421-436.
19. T. Vander, R. Alvarez, M. Ferraro, J. Fohl, K. Hofherr, J.M. Huart, E. Mattila, R. Propson, R. Willmers, and B. Vdvelden, *Coke quality improvement.Possibilities and limitations*, in *3rd International Ironmaking Congress Proceedings*1996: Gent. p. 16-18.
20. G.A. Simons: *Combustion and Flame*, 1983, vol. 53, no. 1-3, pp. 83-92.
21. Y. Kubota, S. Nomura, T. Arima, and K. Kato: *ISIJ international*, 2011, vol. 51, no. 11, pp. 1800-1808.
22. Y. ZhuoZhu, S. Gupta, O. Kerkkonen, R. Kanniala, and V. Sahajwalla: *ISIJ International*, 2013, vol. 53, no. 1, pp. 181-183.
23. T. Yamamoto, K. Hanaoka, S. Sakamoto, I. Shimoyama, K. Igawa, and K. Takeda: *Journal of the Iron and Steel Institute of Japan-Tetsu to Hagane*, 2006, vol. 92, no. 3, pp. 206-212.